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## (54) A SUBSTRATE FOR BIOCHEMICAL REACTIONS

- (71) We, GARY AIRCRAFT CORPORATION, a Corporation organised under the Laws of the State of Texas, United States of America, of P.O. Box 3486, City of San Antonio, State of Texas 78285, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- The present invention pertains to the provision of a substrate for the carrying out of biochemical oxidation-reduction reactions. These reactions are generally carried out in a gas/liquid/solid interface under aerobic or anaerobic reactions. Typical of reactions of this nature are various water treatment processes, methods for treating industrial waste and liquid effluent, sewage treatment processes and the like.
- Liquid effluent and waste water are commonly treated by passage through aerated percolating or trickling filters so that the water is purified by biologically-active micro-organisms attached to packed beds within the filter. These types of filters have been used in ever-increasing numbers due in large part to governmental regulations to protect the environment. For example, the biological oxygen demand (BOD) of waste water is regulated in order that rivers, streams, lakes and other bodies of water remain capable of sustaining life.
- Conventional trickle filters are packed with various media such as, for example, rock, coke, clinker and the like to which the biologically active-micro-organisms become attached. Air necessary for oxidation passes through interstices in the packing medium, and water or liquid to be treated is "trickled" or otherwise passed downwardly through the bed.
- Conventional filter systems have suffered the shortcomings of low throughput, low biological activity and lack of uniform spread of liquid to all parts of the filter medium. In addition, the filter media of conventional systems frequently have failed to offer the biological film a good mechanical and environmental footing where it can grow satisfactorily.
- More recent innovations in trickle and similar type filters are directed to the provision of plastic or organic polymeric filter media in an attempt to increase the surface area of the packing media and improve adhesion of micro-organisms thereto. Typical of these innovations is that disclosed in the patent to Robjohns, issued December 20, 1966, as U.S. Patent No. 3,293,174.
- Improved filter systems such as that disclosed in the Robjohns patent have offered certain advantages such as higher surface area in the filter medium but nonetheless are limited in throughput. For example, organic polymer filter media are susceptible of flow shock whereby excessive volumes of liquid to be treated tend to dislodge or otherwise render ineffective the biological film that has attached itself to the filter media surfaces. In addition, the organic polymeric filter media dry rapidly during periods of non-use which can result in loss of effectiveness of the biological film.
- Filter media used for sewage treatment, trickle filters and the like should meet a number of requirements for satisfactory operation. For example, the medium should be biologically inert, i.e., neither attached by nor inhibiting the growth of the biological organisms which affect the treatment of sewage and reduction of BOD. In addition, the surface of the medium should offer the biological film a good mechanical and environmental footing as previously mentioned. The structural configuration of the medium employed should be such as to promote the uniform spread of liquid to all parts of the available surface of the medium and also should provide for flow of liquid

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thereover in as thin a film as possible in order to allow gas exchange required for biological growth.

In addition to the foregoing, the filter medium or substrate should provide adequate void space to permit a steady supply of air or other gas to be circulated to the biological growth. For sewage application, the void must also allow free passage of the treated effluent downward.

The filter media serving as a substrate should be chemically stable and should not degrade with age. Important to filtration media used in treating industrial effluent is the characteristic of remaining stable in the presence of small quantities of solvents, acids or organic chemicals.

Finally, the filter media should be mechanically stable for purposes of supporting its own weight plus the considerable added weight of the effluent and biological growth. At the same time, the media should be hydrophilic to promote wetting of the total surface by liquid and should retain the liquid to avoid drying during intermittent flow.

According to the present invention a product for use as a substrate for biochemical reactions comprises:—

- (a) rigid porous silica foam, and
- (b) a coating on said foam of an organic polymer.

Preferably the organic polymer of the coating (b) is methyl cellulose, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, or gelatin and may include additionally a nutrient, such as a nitrate, phosphate or a mixture thereof.

The pore size of the rigid porous silica foam is preferably within the range 10 to 300 microns inclusive.

According to another aspect of the invention a method of preparing a product for use as a substrate for biochemical reactions comprises the steps of:—

- (a) foaming and gelling a silica containing material,
- (b) causing or allowing the material formed in step (a) to harden,
- (c) imparting porosity to the hardened material, and
- (d) coating the porous material with an organic polymer.

The coated silica foam of the present invention provides higher surface areas for the substrate than are present in organic foam filters thereby enabling greater throughput. In addition, the silica foam substrate better withstands temperature shock, volume of flow shock, toxicity shock and drying shock as compared with the organic foam materials. For example, the plastic foams are susceptible to degradation because of adverse temperature conditions as well as decomposition due to solvents, acids and the like frequently present in industrial waste.

The silica foam substrate of the present invention exhibits greater capillary action characteristics as compared with organic foam substrates with the consequent advantage that substrates of the present invention do not dry as rapidly during periods of non-use, and the susceptibility of the substrate to poisons that may be present in the liquid material is diminished since water retained in the substrate dilutes the poison rendering it less harmful.

The object of the present invention is a substrate and a method of preparing the substrate for biochemical reactions, that includes the steps of foaming and gelling a silica containing material, causing or allowing the material to harden, imparting porosity to the hardened material and coating the porous material with an organic polymer.

The silica foam substrate of the present invention may be manufactured by the method disclosed in U.S. Patents Nos. 1,944,008 and 1,944,007 assigned to Battelle Memorial Institute by Floyd B. Hobart for a "Heat Insulating Material and Method for Making Same" and a "Light Weight Ceramic Material and Method for Making Same", respectively, followed by washing with hot water to remove water soluble materials from the pores of the silica.

Another useful silica foam is manufactured by Fiberglas Canada Limited. The foam is prepared from an alkali metal silicate such as sodium silicate or potassium silicate wherein the alkali metal to silicate ratio is high enough for solubility purposes. A suitable gelling agent is added to the silicate gradually to increase polymerization of the silicate to effect gelation. The material is foamed such as by use of a high shear impeller device in mechanical whipping action or by forcing compressed air or other gas into the body of liquid. Small amounts of foaming agents greatly enhance foaming action. These agents must be soluble in the material and compatible therewith. Saponin, Rosin soap and soap bark are normally used. The gelling agent may be added either during foaming or afterwards, following which the foam is caused or allowed to harden. Hardening of the foam to a rigid mass is a function of time, temperature and pH. Temperature and pH change must be gradual to avoid fracture or crystallization into particles. Control of pH change may be effected by use of a gelling agent of limited solubility or by use of a gelling agent which is of a different phase, either gas or liquid. Boric acid and carbon dioxide gas may be used. After hardening the resulting silica foam has porosity imparted thereto, for example by etching or leaching. This process may be carried out by contacting the foam with hot water. Small amounts of strong acids such as hydrochloric or sulphuric may be used or larger

amounts of weak Lewis Acids may be used to accelerate leaching. The porous foam is then dried resulting in a rigid porous material.

5 The rigid silica foam blocks or pieces of desired shape are then coated with an organic polymer. The organic polymer selected should advantageously be capable of swelling and becoming viscous in contact with water. While the strength of the organic polymer is not critical, the organic polymer solution used to coat the silica foam should not be so viscous as to clog the silica foam pores. Consequently, coating solutions containing 0.5 to 5% of organic polymer are preferred although higher concentrations may be used. The preferred organic polymer for coating silica foam according to the present invention is polyvinyl alcohol because of its characteristics of adhering to the silica foam surfaces even in dilute solutions.

20 Nutrients may be added to the organic polymer material used to coat the silica foam to enhance or modify as desired the biological activity of the filter media. For example, ammonium nitrate and/or tripotassium phosphate may be added to the organic polymer solution in desired amounts. Applicants have discovered that a suitable nutrient-organic polymer coating solution may contain 2% polymer, 0.1% ammonium nitrate, 0.2% tripotassium phosphate, and 97.7% water (expressed in weight percentages). Of course, these proportions may be varied and other nutrients may be used as will be appreciated by those skilled in the art.

35 In typical applications such as a biofilter or trickle filter, the rigid plastic coated silica foam blocks are preferably firmly bonded to a plastic bottom or base in the enclosure vessel of the filter such as by means of a suitable adhesive to form a strong, chemically-resistant base.

40 Then the plastics coated foam blocks are stacked in layers one on the other as previously described. Because of the lightweight, low density characteristics of the silica foam, beds of ten feet or more may be prepared without the necessity of intermediate supports. When intermediate supports are necessary simple plastic beams suitably spaced may be used for supporting tall stacks of the filter media. Thus, it now will be recognized that significant weight saving is inherent in the present invention to enable the design of filters of any height. In addition, it is possible to carry out separate treatment operations in structures of selected lengths or heights with introduction of liquid to be treated and oxygen at selected concentrations and levels.

60 The silica foam is coated with an organic polymer so as to convert the foam pores or cells into sites almost immediately suitable for bacterial growth. For example, and as will be explained hereafter, if the silica foam is

flushed and coated with gelatin or a polymer such as methyl cellulose, polyvinyl pyrrolidone, polyvinyl alcohol or polyvinyl acetate, hydrophilic properties of the silica foam are increased enabling the silica foam substrate to be washed with waste water and to be quickly covered by biological films. On the other hand, if untreated silica foam is placed in a trickle filter, up to three weeks may be required before bacteria or biological films develop to the extent that the trickle filter may effectively oxidize the waste liquid.

70 The pore size of the silica foam as described above ranges from ten to 300 microns inclusive. While not critical, pores in this range of size provide a relatively enormous surface area as compared with conventional trickle filters thereby promoting high throughput through the filter and high conversion rates from the standpoint of oxidation or organic materials contained in the material to be treated.

#### Example 1

90 A trickle filter was prepared having a packed bed comprised of silica foam blocks of the type previously described with respect to Fiberglas Canada Limited Dimensions of the silica foam blocks were two inches by ten inches, weighing four to five pounds per cubic foot. Prior to use, the silica foam material was coated with polyvinyl alcohol to enhance the hydrophilic character of the foam and withstand washing by waste water long enough for the substrate to be covered by biologically produced polymers as previously explained. The polyvinyl alcohol solution was 2% by weight polyvinyl alcohol in 98% water, the foam blocks having been flushed with the solution and allowed to drain and dry in air.

100 The treated silica foam blocks were placed on rock filter media in a conventional trickle filter and waste water was trickled over the bed. One week later, the silica foam was noticeably greener with algae than the conventional rock filter media. Part of the foam was cut in two and examined microscopically evidencing filamentous and gelatinous growth. One year later, the silica foam blocks in the trickle filter were still obviously greener with algae than the surrounding conventional rock filter media when viewed from a distance of several feet. Microscopic examination of the interior of one silica foam block exhibited slightly more filamentous and gelatinous mass than the one-week sample, although water flowed readily through the silica foam material.

#### Example 2

105 To demonstrate effectiveness of the silica foam as a substrate for treating industrial waste, a biological treatment column was prepared by stacking silica foam blocks of the nature explained in Example 1 in a vessel. Dimensions of the blocks were two

inches by eighteen inches by eighteen inches. the blocks being stacked in rows, each row being stacked at right angles with respect to the next row. The approximate volume of foam used was 50 cubic feet which occupied a filter volume of 100 cubic feet. The silica foam material was treated with an organic polymer prior to use in a manner similar to that explained in Example 1 except that the polymer was methyl cellulose sold under the trade name "Methocel 65HG" (Registered Trade Mark) by Dow Chemical Co. Industrial waste water was circulated and recirculated through the filter at an average flow of 390 gallons per cubic foot per day. After the filter had been in operation only three days, average reduction of BOD was 29%, in one pass. Average reduction of cyanide in the 0.1 to 4 parts per million range was 90%. Phenol reduction was 48%.

#### Example 3

Two biological treatment columns were prepared by stacking blocks of silica foam blocks with dimensions of two inches by eighteen inches by eighteen inches in filter vessels, the silica foam being of the nature described in Example 1. The volume of foam in each column was 100 cubic feet occupying a total volume of 200 cubic feet each. The silica foam in one column was not treated with organic polymer while the silica foam in the second column was treated with good grade gelatin in the manner described in Example 1. Industrial waste water was passed through both filters at a rate of 216 gallons per cubic foot of silica foam media per day. In the column having silica foam treated with gelatin, reduction of BOD of the industrial waste water began after only two days and average BOD reduction in the first three weeks of operation of such filter was 56%. In the column having silica foam untreated with organic polymer, BOD reduction began after ten days and average BOD reduction in a three-week period beginning 17 days from inception was 47%.

Comparing the foregoing examples of silica foam trickle filter treatment of industrial waste water with conventional high rate trickle filters, conventional high rate trickle filters are capable of reducing BOD 50% to 70%, at a flow rate of 15 gallons per cubic foot per day. In contrast, the use of silica foam filters (even without organic polymer coating) reduced BOD from about 25% to nearly 60% at flow rates of 15 to 20 times of that of conventional filters. Consequently, the use of inorganic foam substrate-type trickle filters is nearly 10 times more effective than conventional biological filters.

#### Example 4

To illustrate effectiveness of silica foam as a filter media for use under anaerobic conditions, a biological treatment column was prepared by stacking silica foam blocks

having dimensions of two inches by eighteen inches by eighteen inches and four to five pounds per cubic foot density in an arrangement whereby the blocks were stacked in rows, one row being at right angles relative to the next. The blocks were placed as close as possible to one another in an effort to leave no spacing between blocks. Prior to use, the silica foam material was treated with polyvinyl pyrrolidone (sold under the trade name "PVP 50" by GAF Corp.) in a manner similar to that explained in Example 1.

Industrial waste water was recirculated through the filter at an average flow of 200 gallons per cubic foot of silica foam per day, the recirculated waste water containing less than 0.01 milligrams per litre of sulphide. After three weeks of operation, cores were taken from the filter bed by driving a one-inch pipe through the foam filter. Core samples of individual blocks were crushed to expel water and the water analyzed for sulphide. Sulphide was found in concentrations up to 0.8 milligrams per litre indicating that anaerobic reduction of sulphates to sulphides had occurred.

The silica foam of the present invention is used in processes described in our copending United Kingdom Patent Applications 59038/71, 48126/73 and 48128/73 (Serial Nos. 1,412,587, 1,412,588 and 1,412,590).

#### WHAT WE CLAIM IS:—

1. A product, for use as a substrate for biochemical reactions, comprising:
  - (a) rigid porous silica foam, and
  - (b) a coating on said foam of an organic polymer.
2. A product, as claimed in Claim 1, wherein the organic polymer of the coating (b) is methyl cellulose, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, or gelatin.
3. The product, as claimed in either of Claims 1 and 2, wherein the coating (b) includes additionally a nutrient.
4. The product, as claimed in Claim 3, wherein the nutrient is a nitrate, phosphate or a mixture thereof.
5. The product, as claimed in any one of Claims 1 to 4, wherein the pore size of the rigid porous silica foam is within the range 10 to 300 microns inclusive.
6. A method, of preparing a product for use as a substrate for biochemical reactions, which comprises the steps of:
  - (a) foaming and gelling a silica containing material,
  - (b) causing or allowing the material formed in step (a) to harden,
  - (c) imparting porosity to the hardened material, and
  - (d) coating the porous material with an organic polymer.
7. The method of Claim 6 wherein, in

step (c), the porosity imparted results in pore size within the range 10 to 300 microns inclusive.

8. The method of either of Claims 6 and 7 wherein the organic polymer for the coating step (d) is methyl cellulose, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, or gelatin.

9. The method of any one of Claims 6 to 8 wherein a nutrient is contained in the organic polymer of step (d). 10

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